Le spectre RMN ^{1}H de (1*a*) présente un hydrogène fortement déblindé (massif à 3,05 p.p.m.). Nous pensons qu'il s'agit de l'hydrogène équatorial H(9). Cette interprétation s'accorde bien avec la liaison hydrogène entre le NH et le fluor mise en évidence par diffraction aux rayons X puisqu'elle amène le carbonyle du groupement acétamido à proximité de cet hydrogène. De plus, par double irradiation homonucléaire, on met en évidence que l'hydrogène, donnant son signal à 3,05 p.p.m., est couplé avec le fluor avec une constante de l'ordre de 8 Hz, ce qui est tout à fait compatible avec une constante $^4J_{F(éq)H(éq)}$ (Jonas, Gutowsky & Allerhand, 1965).

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N-Acetyl-L-tyrosine

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Abstract. $C_{11}H_{13}NO_4$, monoclinic, $P2_1$, $a = 5{\cdot}934$ (2), $b = 7{\cdot}391$ (3), $c = 12{\cdot}488$ (6) Å, $\beta = 101{\cdot}19$ (3)°, $V = 537{\cdot}3$ Å^3 (all at 138 ± 2K), $a = 5{\cdot}994$ (6), $b = 7{\cdot}495$ (2), $c = 12{\cdot}510$ (5) Å, $\beta = 101{\cdot}77$ (6)° [all at 296 (2)K]; $Z = 2$, $M_r = 223{\cdot}23$, D_x [296 (2)K] = 1·347, $D_m = 1{\cdot}344$ Mg m^{-3}. All intensity data were collected at 138 ± 2K. The final R value is 0·030 for all 1196 reflections. The crystal is stabilized by extensive intermolecular hydrogen bonding involving all N and O atoms. This compound differs from other structures of aromatic amino acids in that ψ^1 [N–C(1)–C(2)–O(1)] = 154° (*trans*) as opposed to the more common values near 0° (*cis*).

Introduction. The structure determination of *N*-acetyl-L-tyrosine was undertaken in order to compare its conformation with other aromatic amino acids and their derivatives.

The compound was purchased from Cyclo Chemical Corporation and was used without further purification. Large, clear, rod-shaped crystals were obtained by slow cooling of an aqueous solution. A crystal 0·43 × 0·17 × 0·13 mm was used for data collection and unit-cell determination at 138 ± 2K using a Nonius CAD-4 automatic diffractometer controlled by a PDP8/e computer. The unit-cell dimensions were determined by a least-squares refinement of 48 reflections chosen from all octants of reciprocal space using Cu $K\alpha_1$ radiation (λ = 1·5405 Å). The intensities of all 1196 independent reflections with $2\theta \leq 150°$ were measured using θ–2θ scans with variable scan rates and Cu $K\bar{\alpha}$ radiation (λ = 1·5418 Å). The scan range and receiving-aperture width were (0·85 + 0·14 tan θ)° and (3·00 + 0·86 tan θ) mm respectively. The maximum scan time per reflection was 75s. For each reflection two thirds of the time was used in scanning the peak (P) and a sixth of the time in scanning each of the left and right backgrounds (LB and RB). The unscaled intensity was calculated by $I = P - 2(\text{LB} + \text{RB})$. The intensities of three monitor reflections were checked after every 5000 s of X-ray exposure and their net counts did not alter significantly over the course of data collection. Three orientation-control reflections were checked after every 200 measurements and no angular change larger than 0·1° was detected and, therefore, no reorientation was performed. Reflections with $I < 2\sigma(I)$ were assigned intensities equal to $1{\cdot}4\sigma(I)$.

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Lorentz and polarization corrections were applied but no absorption correction was made. Each structure amplitude was assigned a weight determined from $\sigma(I)$ and based on counting statistics and intensity (Ealick & van der Helm, 1975).

The structure was solved by direct methods (Karle & Karle, 1966) using the *MULTAN* program (Germain, Main & Woolfson, 1971) and was refined isotropically to $R = \sum|(|kF_o| - |F_c|)|/\sum|kF_o| = 0{\cdot}084$. All H atoms were located from a difference Fourier map based on the partially refined positions of the C, N and O atoms. Further refinement was carried out with anisotropic thermal parameters for C, N and O atoms and isotropic thermal parameters for H atoms. Refinement was discontinued when all parameter shifts were less than a third of their corresponding standard deviations. The final R factor for all reflections is 0·030 while the goodness of fit is 1·08.

In all refinements a block-diagonal least-squares program (Ahmed, 1966) was used (9 × 9) in which the quantity $\sum w_f(|kF_o| - |F_c|)^2$ was minimized. The scattering factors for C, N and O atoms were taken from *International Tables for X-ray Crystallography* (1974) and those for H atoms from Stewart, Davidson & Simpson (1965).

Discussion. A stereoview of a single molecule is shown in Fig. 1 and positional parameters are listed in Tables 1 and 2.* Bond distances and atom labeling are shown in Fig. 2 while bond angles involving non-hydrogen atoms are listed in Table 3. The phenolic ring is quite planar with all atoms deviating less than 0·003 Å from the least-squares plane.

Conformational angles, following the convention of the IUPAC–IUB Commission on Biochemical Nomenclature (1970) and the nomenclature of Winkler & Dunitz (1971), are listed in Table 4. These angles yield for the three independent parameters of the amide group, χ_C $[=\omega_1 - \omega_3 + \pi(\text{mod } 2\pi)]$, χ_N $[=\omega_2 - \omega_3 + \pi(\text{mod } 2\pi)]$ and τ $[=\frac{1}{2}(\omega_1 + \omega_2)$, and $|\omega_1 - \omega_2| < \pi]$ −1·5 (3), 14·1 (21) and 176·9 (10)° respectively, where the standard deviation for the last digit is given in

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35814 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

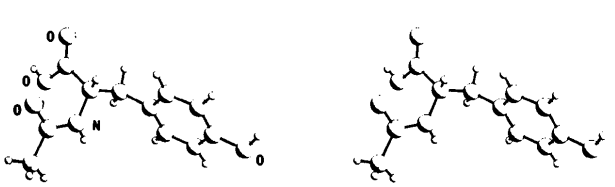

Fig. 1. Stereoview of *N*-acetyl-L-tyrosine.

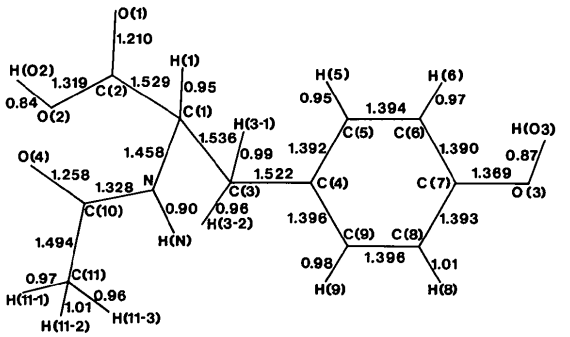

Fig. 2. Atom numbering and bond distances (Å) in *N*-acetyl-L-tyrosine. The standard deviation for the bonds involving non-hydrogen atoms is 0·002 Å, while it is 0·02–0·03 Å for those involving H atoms.

Table 1. *Positional parameters* (×10⁵) *and equivalent isotropic thermal parameters* (Å² ×10⁴) *for* C, N *and* O *atoms*

Standard deviations for the last digits are in parentheses.

	x	y	z	U^*_{eq}
C(1)	45174 (24)	107039 (22)	22510 (11)	172 (6)
C(2)	57284 (25)	103576 (22)	12957 (11)	179 (6)
C(3)	38614 (27)	88731 (23)	26867 (12)	209 (6)
C(4)	31900 (25)	89971 (23)	38001 (11)	183 (6)
C(5)	47215 (26)	97161 (23)	46836 (12)	192 (6)
C(6)	42091 (27)	97177 (23)	57264 (12)	205 (6)
C(7)	21359 (26)	90054 (23)	58916 (11)	191 (6)
C(8)	5827 (24)	82779 (25)	50166 (13)	213 (6)
C(9)	11118 (26)	82870 (24)	39749 (12)	204 (6)
C(10)	25889 (25)	134393 (24)	14794 (11)	183 (6)
C(11)	3853 (28)	143598 (28)	9931 (13)	270 (7)
N	24738 (21)	118242 (20)	19325 (10)	186 (5)
O(1)	77631 (18)	100347 (20)	14318 (9)	250 (5)
O(2)	43196 (19)	103753 (22)	3390 (9)	268 (5)
O(3)	15498 (19)	89991 (20)	68995 (8)	247 (5)
O(4)	44999 (18)	141493 (19)	14422 (8)	210 (5)

* $U_{eq} = \frac{1}{6}\pi^2 \sum_i \sum_j \beta_{ij} \mathbf{a}_i . \mathbf{a}_j$.

Table 2. *Positional parameters* (×10³) *and thermal parameters for* H *atoms*

	x	y	z	B (Å²)
H(1)	560 (3)	1134 (3)	278 (1)	1·1 (3)
H(3-1)	527 (4)	812 (4)	273 (2)	3·3 (5)
H(3-2)	265 (4)	834 (3)	216 (2)	2·0 (4)
H(5)	615 (3)	1020 (3)	459 (2)	1·7 (4)
H(6)	536 (4)	1015 (4)	633 (2)	2·1 (4)
H(8)	−89 (3)	773 (4)	515 (2)	1·7 (4)
H(9)	7 (4)	770 (4)	337 (2)	2·3 (4)
H(11-1)	38 (4)	1465 (4)	23 (2)	3·7 (6)
H(11-2)	−101 (4)	1359 (4)	102 (2)	3·3 (5)
H(11-3)	29 (5)	1548 (5)	137 (2)	4·4 (6)
H(N)	108 (4)	1131 (4)	190 (2)	3·3 (5)
H(O2)	497 (5)	1010 (4)	−18 (2)	3·3 (5)
H(O3)	276 (4)	917 (4)	741 (2)	2·8 (4)

Table 3. *Bond angles* (°)

The estimated standard deviation for all angles is 0·1°.

C(2)–C(1)–N	112·0	C(5)–C(6)–C(7)	119·9
C(2)–C(1)–C(3)	108·6	C(6)–C(7)–C(8)	120·0
C(3)–C(1)–N	110·0	C(7)–C(8)–C(9)	119·7
O(1)–C(2)–C(1)	122·1	C(8)–C(9)–C(4)	120·8
O(2)–C(2)–C(1)	113·2	O(3)–C(7)–C(6)	121·9
O(2)–C(2)–O(1)	124·7	O(3)–C(7)–C(8)	118·2
C(1)–C(3)–C(4)	113·6	C(1)–N–C(10)	121·2
C(3)–C(4)–C(9)	121·1	N–C(10)–O(4)	120·8
C(3)–C(4)–C(5)	120·1	O(4)–C(10)–C(11)	121·2
C(9)–C(4)–C(5)	118·7	N–C(10)–C(11)	118.0
C(4)–C(5)–C(6)	120·9		

Table 4. *Conformational angles* (°)

C(11)–C(10)–N–C(1)	ω_1	169·1 (1)
O(4)–C(10)–N–H(N)	ω_2	−175·3 (19)
O(4)–C(10)–N–C(1)	ω_3	−9·4 (2)
C(11)–C(10)–N–H(N)	ω_4	3.2 (19)
C(10)–N–C(1)–C(2)	φ	−55·8 (2)
N–C(1)–C(2)–O(1)	ψ^1	153·9 (2)
N–C(1)–C(2)–O(2)	ψ^2	−28·7 (2)
C(4)–C(3)–C(1)–N	χ^1	−71·5 (1)
C(9)–C(4)–C(3)–C(1)	χ^{21}	127·0 (2)
C(5)–C(4)–C(3)–C(1)	χ^{22}	−57·4 (2)

parentheses. The amide group is *trans* and its non-planarity is primarily due to the pyramidality of the three bonds attached to the N atom ($\chi_N \neq 0$).

The other conformational angles are similar to those of other aromatic amino acid derivatives (Cody, Duax & Hauptman, 1973; Michel & Durant, 1976) and of aromatic amino acids in protein structures (Janin, Wodak, Levitt & Maigret, 1978) with the exception of ψ^1. The χ^1 angle of −71·5° for this structure places the side chain in the g^+ position (*trans* to the carboxyl group) (Janin *et al.*, 1978) or class *C* (Cody *et al.*, 1973) and is close to the mean value. The χ^2 angle of 127·0° is significantly larger than the mean (92°), but is within the range of known structures and is consistent with class *C*. Further designation of this compound as class C_1 or C_2 is difficult due to the unusual value of ψ^1. In the acid salts of aromatic amino acids where a distinction can be made between the hydroxyl and carboxyl oxygens, and in the amino acid esters, the ψ^1 value (N–C^α–C^1=O) is always relatively close to 0°, and the carboxyl O is thus approximately

Table 5. *Hydrogen bonds*

	D	*A*	*D*–*A*	*D*–H	*A*–H	*D*–H–*A*
A	O(3)	O(4)^{i}	2·813 (1) Å	0·87 (2) Å	1·95 (2) Å	171 (2)°
B	N	O(1)^{ii}	3·045 (2)	0·90 (3)	2·16 (3)	167 (2)
C	O(2)	O(4)^{iii}	2·620 (2)	0·84 (3)	1·81 (3)	162 (3)

Symmetry code: (i) $1-x, y-\frac{1}{2}, 1-z$; (ii) $x-1, y, z$; (iii) $1-x, y-\frac{1}{2}, -z$.

cis to the N atom. In the present structure, however, the carboxyl oxygen [O(1)] is approximately *trans* to the N atom (ψ^1 = 153·9°). The cause for this unusual conformation is probably the hydrogen bond *B* (Table 5) in which the N atom acts as a donor and O(1) of the translation-related molecule along *a* acts as acceptor, which results in H-bonded molecular chains along *a*. The bond distances in the molecule are normal with the exception of the rather long distance for C(10)–O(4) (1·258 Å), while a more normal value of 1·23–1·24 Å can be expected in amide bonds. The reason for the lengthening may be the fact that O(4) is the acceptor for two strong hydrogen bonds, listed in Table 5 (H-bonds *A* and *C*).

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